

# PATENT ABSTRACTS OF JAPAN

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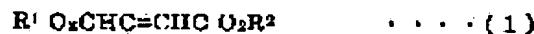
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## (54) ORGANIC PEROXIDE SOLUTION AND MANUFACTURING METHOD OF VINYL CHLORIDE POLYMER USING THE SAME

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide an organic peroxide composition wherein a solvent of an organic peroxide used as a polymerization initiator imparts no influence to physical properties of a vinyl chloride polymer after polymerization or a molding process thereof, and hardly volatilizes nor elutes from the vinyl chloride polymer, the composition being friendly to the environment and improving productivity of the polymer, and to provide a manufacturing method of the vinyl chloride polymer using the composition.

SOLUTION: The organic peroxide composition comprises the organic peroxide and a compound represented by formula (1) (wherein R1 and R2 are each a 1-8C alkyl group) as the solvent for the organic peroxide.



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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] This invention relates to the organic peroxide solution used in order to manufacture a vinyl chloride system polymer. In detail a vinyl chloride system polymer A film, a sheet, a pipe, a plate, The solvent of the organic peroxide used as a polymerization initiator in case it casts for applications, such as a corrugated plate, a joint, a leather, covering material of lead wire, flooring, fiber, and autoparts, is hardly volatilized and eluted. Moreover, the solvent of the organic peroxide used as a polymerization initiator also in mold goods is related with the manufacture approach of the organic peroxide solution which can offer the vinyl chloride system polymer hardly volatilized and eluted, and the above-mentioned vinyl chloride system polymer using it.

**[0002]**

[Description of the Prior Art] Generally as a polymerization initiator at the time of manufacturing a vinyl chloride system polymer, organic peroxide is used. Since much of the organic peroxide is sensitive to an impact, organic peroxide is diluted with a solvent in order to deal with it safely. Transport, It is using. As the diluent, as an aliphatic series system hydrocarbon solvent For example, shell ZORU (made in SHIERU Chemicals Japan), Toluene, ethylbenzene, etc. are used as Isopar (product made from Esso Chemistry), Nippon Oil eye SOZORU (product made from Nippon Oil Chemistry), IP solvent (product made from Idemitsu Petrochemistry), etc. and an aromatic series system hydrocarbon solvent. However, this has had bad effect on the quality, work environment, and productivity of organic peroxide as a polymerization initiator. For example, since the above-mentioned solvent currently used conventionally is volatilized and eluted, is volatilized eluted after molding from mold goods at the time of vinyl chloride system polymer molding and remains in mold goods at it at the time of molding, stickiness arose to molding equipment, it had to fix periodically, and manufacture has interrupted it each time.

**[0003]**

[Problem(s) to be Solved by the Invention] As mentioned above, when an aliphatic series system hydrocarbon and an aromatic series system hydrocarbon are used as a solvent, although the solvent influences neither a polymerization nor quality, it will be volatilized and eluted from the time of molding, and mold goods. Even if it is dramatically difficult to remove since it is retarder thinner even if it is going to remove these solvents and it tends to remove, there is a limitation. Moreover, since this solvent is volatilized eluted from mold goods and toluene, ethylbenzene, etc. are contained in waste fluid as the activity is regulated by the law (PRTR law) about acceleration of an improvement of managements, such as grasp of the discharge to the environment of specified chemical substances, they do an adverse effect to an environment. Moreover, since the solvent remains in mold goods at the time of molding, stickiness arises to molding equipment, and productivity is reduced. And the solution policy is not conventionally shown to such a technical problem. It is the technical problems of this invention to offer the organic peroxide solution which can manufacture the vinyl chloride system polymer with which the quality of a polymerization reaction or mold goods was not affected, and volatilization of the solvent from the time of molding and mold goods and elution were reduced, and loses stickiness of molding equipment, and raises productivity from such a viewpoint, and to offer the manufacture approach of the vinyl chloride system polymer by it.

[0004]

[Means for Solving the Problem] By using the compound shown by the following general formula (1) as a solvent of organic peroxide, as a result of inquiring wholeheartedly so that this invention persons may aim at solution of the above-mentioned technical problem Can deal with organic peroxide sensitive to an impact safely, and neither a polymerization nor quality is affected. It found out that productivity could be raised by reducing volatilization and elution of the solvent from the time of molding, and mold goods, and reducing the amount of solvents which remains in mold goods further, and losing stickiness of molding equipment. That is, this invention relates to the organic peroxide constituent which uses as a content solvent organic peroxide and the compound shown by the following general formula (1) as a solvent for this organic peroxide.

[0005]

[Formula 4]



[0006] (R1 and R2 show the alkyl group of carbon numbers 1-8 among a formula, respectively.) This invention relates to the organic peroxide solution which comes to dissolve organic peroxide in the compound shown by the above-mentioned general formula (1) again. Furthermore, this invention relates also to the manufacture approach of the vinyl chloride system polymer characterized by carrying out the polymerization of the monomer which copolymerization is carried out to a vinyl chloride monomer or a vinyl chloride monomer, and this, and is sold to the bottom of existence of the organic peroxide solution which comes to dissolve organic peroxide in the compound of the above-mentioned general formula (1).

[0007]

[Embodiment of the Invention] Below, the operation gestalt of this invention is explained at a detail. As a solvent for organic peroxide, the compound expressed with a general formula (1) is used. As an alkyl group of the carbon numbers 1-8 in a general formula (1), methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, n-octyl, and 2-ethylhexyl are illustrated. As a compound shown by the general formula (1), both the types of a maleic acid and boletic acid are included. As an example of the compound shown by the general formula (1) Dimethyl maleate, diethyl maleate, dipropyl maleate, Dibutyl maleate, dipentyl maleate, dihexyl maleate, Diheptyl maleate, G n-octyl maleate, G 2-ethylhexyl maleate, Although dimethyl fumarate, diethylfumarate, dipropyl fumarate, dibutylfumarate, dipentyl fumarate, dihexyl fumarate, diheptyl fumarate, G n-octyl fumarate, G 2-ethylhexyl fumarate, etc. are mentioned It is not limited to these. These solvents can be used by the concentration which may dissolve organic peroxide, and the concentration of organic peroxide is more preferably used at 20 - 80 % of the weight ten to 90% of the weight.

[0008] In this invention with a vinyl chloride system polymer The homopolymer of a vinyl chloride monomer, As a monomer by which a copolymer is mentioned and copolymerization is carried out to a vinyl chloride monomer, or for example, ethylene, A propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecen, Alpha olefins, such as 1-tridecanoic and 1-tetra-decene, an acrylic acid, An acrylic acid or its ester, such as a methyl acrylate and an ethyl acrylate, A methacrylic acid or its ester, such as a methacrylic acid and a methyl methacrylate, Although vinyl ether, such as vinyl ester, such as a maleic acid or its ester, vinyl acetate, and propionic-acid vinyl, lauryl vinyl ether, and isobutyl vinyl ether, a maleic anhydride, acrylonitrile, a vinylidene chloride, styrene, etc. are mentioned It is not limited to these. These are used in independent or two or more sorts of combination.

[0009] If it is the organic compound used as a polymerization initiator as organic peroxide in this invention, there will be especially no definition. As peroxy ester 3-hydroxy - 1 and 1-dimethyl butylperoxyneodecanoate, Alpha-cumilperoxy neodecanoate, a G t-hexyl peroxy JIGURIKO rate, T-butylperoxy neodecanoate, t-amyl peroxy neo decanoate, T-hexylperoxy neodecanoate, 1, 1 and 3, 3-tetramethyl butylperoxyneodecanoate, 1, 1, 3, and 3-tetramethylbutyl peroxy neoheptanoate, t-butyl par OKISHINEO hexanoate, t-amyl peroxy neo hexanoate, t-hexyl peroxy neo hexanoate, t-butylperoxy perpivalate, t-amyl peroxy pivalate, t-hexyl peroxy pivalate, t-butyl peroxy neoheptanoate, t-amyl peroxy neoheptanoate, t-hexyl peroxy neoheptanoate, tert-butyl peroxide-2-methyl-2-isopropyl butyrate, t-amyl peroxy-2-methyl-2-isopropyl butyrate, t-hexyl peroxy-2-methyl-

2-isopropyl butyrate, t-octyl peroxy-2-methyl-2-isopropyl butyrate, 1-methyl -1 - Cyclohexyl ethyl peroxy-2-methyl-2-isopropyl butyrate, cumyl peroxy-2-methyl-2-isopropyl butyrate, etc. are mentioned. As peroxy dicarbonate Diisopropyl peroxy dicarbonate, di(2-ethylhexyl) peroxy dicarbonate, II (secondary butyl) peroxy dicarbonate, G 4-t-butyl cyclohexyl peroxy dicarbonate, Dimyristyl peroxy dicarbonate, JI (2-ethoxyethyl) peroxy dicarbonate, Di-n-propyl peroxy dicarbonate, JI (3-methoxy butyl) peroxy dicarbonate, etc. are mentioned. As diacyl peroxide Although JIRAU roil peroxide, JISO butyryl peroxide, JI (3, 5, and 5-trimethylhexanoyl) peroxide, etc. are mentioned, it is not limited to these. These can be used together with independent or two or more sorts of two or more organic peroxide.

[0010] There is especially no constraint, the approach by the gestalt of mass, suspension, emulsification, micro suspension, a solution, etc. is mentioned, and although the polymerization method of the vinyl chloride system polymer in this invention is a suspension-polymerization method preferably, it is not limited to this. The distributed assistant currently generally used in the technical field concerned in the suspension-polymerization method, For example, methyl cellulose, hydroxyethyl cellulose, hydroxypropylcellulose, Water-soluble cellulose ether, such as hydroxypropyl methylcellulose, The partial saponification polyvinyl alcohol of water-soluble or oil solubility, an acrylic-acid polymer, Water soluble polymers, such as gelatin, sorbitan monolaurate, a sorbitan trio rate, Oil solubility emulsifiers, such as glycerol tristearate and an ethylene oxide propylene oxide block copolymer, Water-soluble emulsifiers, such as polyoxyethylene sorbitan monolaurate, polyoxyethylene glycerol olate, and lauric-acid sodium, etc. can also be used in one sort or two sorts or more of combination. Furthermore, by this polymerization system, it is also arbitrary to add the modifier suitably used for the polymerization of a vinyl chloride system, a chain transfer agent, pH regulator, a gelation amelioration agent, an antistatic agent, a cross linking agent, a stabilizer, a bulking agent, an antioxidant, a buffer, a scale inhibitor, etc. if needed.

[0011] the amount of the organic peroxide used, i.e., a polymerization initiator, -- the vinyl chloride system monomer 100 weight section -- receiving -- pure article conversion -- 0.001 - 2 weight section -- it is 0.001 - 1 weight section preferably. Under in the 0.001 weight section, if a rate of polymerization falls and 2 weight sections are exceeded, a rate of polymerization will become large and the control will become difficult.

[0012] Polymerization temperature changes with combination of a polymerization method or a monomer, and although it is not uniform, it is 30-70 degrees C preferably 10-80 degrees C. At less than 10 degrees C, it is in the inclination for polymerization time amount to become long, and the conclusion of a reaction is difficult, polymerization time amount becomes long, and productivity falls. It becomes [ a reaction rate becomes remarkably large, control of a polymerization reaction becomes difficult, the life of a polymerization initiator becomes short, and / reaching a high invert ratio ] difficult and is not desirable if it exceeds 80 degrees C.

[0013]

[Working Example(s) and Comparative Example(s)] Although an example and the example of a comparison are shown below and this invention is explained concretely, this invention is not limited to these examples.

[0014] 1300ml of ion exchange water and polyvinyl alcohol 0.8g were put into the autoclave made from stainless steel of 2L, it dissolved in it, then, the 36.5 ppm organic peroxide constituent (after-mentioned) was added with the active oxygen base, nitrogen gas fully permuted the inside of an autoclave, and after that, the inside of an autoclave was made into the vacuum and sealed. The autoclave was filled up after heating 650g of vinyl chloride monomers. After it performed a polymerization and a pressure declined by 0.5 atmospheric pressures, warming an autoclave with warm water and keeping internal temperature at 57 degrees C, the polymerization was terminated 1 hour after. The autoclave was cooled after polymerization termination, and after 300ml ion exchange water washed the obtained white crystal twice except for the unreacted vinyl chloride monomer, it dried at 50 degrees C. The result of having performed measurement of the ullage of a solvent, a polymerization invert ratio, and bulk specific gravity was shown in a table 1.

[0015] It adds to a 100ml tetrahydrofuran and 5g of vinyl chloride polymers obtained by carrying out [ullage of solvent] desiccation is dissolved thoroughly. the tetrahydrofuran solution with which the vinyl chloride polymer dissolved completely -- gas chromatography -- analyzing -- a vinyl chloride

polymerization -- the solvent content in the living body was computed.

[0016] 796 ppm of dibutyl maleate 70% solutions of t-butylperoxy neodecanoate were added to the vinyl chloride monomer as a [example 1] organic peroxide constituent, and the polymerization was performed.

[0017] 1130 ppm of dibutyl maleate 70% solutions of di(2-ethylhexyl) peroxy dicarbonate were added to the vinyl chloride monomer as a [example 2] organic peroxide constituent, and the polymerization was performed.

[0018] 620 ppm of dibutyl maleate 70% solutions of 450 ppm and di(2-ethylhexyl) peroxy dicarbonate were added for the dibutyl maleate 70% solution of alpha-cumilperoxy neodecanoate to the vinyl chloride monomer to the vinyl chloride monomer, respectively as a [example 3] organic peroxide constituent, and the polymerization was performed.

[0019] It is 3-hydroxy as a [example 4] organic peroxide constituent. - 620 ppm of dibutyl maleate 70% solutions of 590 ppm and di(2-ethylhexyl) peroxy dicarbonate were added for the dibutyl maleate 50% solution of 1 and 1-dimethyl butylperoxyneodecanoate to the vinyl chloride monomer to the vinyl chloride monomer, respectively, and the polymerization was performed.

[0020] 70% solution of aliphatic series system hydrocarbons of t-butylperoxy neodecanoate was added instead of the organic peroxide constituent of the [example 1 of comparison] example 1, and the polymerization was performed.

[0021] 70% solution of aliphatic series system hydrocarbons of di(2-ethylhexyl) peroxy dicarbonate was added instead of the organic peroxide constituent of the [example 2 of comparison] example 2, and the polymerization was performed.

[0022] 70% solution of aliphatic series system hydrocarbons of alpha-cumilperoxy neodecanoate and 70% solution of aliphatic series system hydrocarbons of di(2-ethylhexyl) peroxy dicarbonate were added instead of the organic peroxide constituent of the [example 3 of comparison] example 3, and the polymerization was performed.

[0023] 50% solution of 3-hydroxy aliphatic series system hydrocarbons of -1 and 1-dimethyl butylperoxyneodecanoate and 70% solution of aliphatic series system hydrocarbons of di(2-ethylhexyl) peroxy dicarbonate were added instead of the organic peroxide constituent of the [example 4 of comparison] example 4, and the polymerization was performed.

[0024]

[A table 1]

	重合体中の溶剤 残存量[ppm]	重合転化率 [%]	かさ比重 [g/ml]
実施例 1	2	84.3	0.475
実施例 2	1	89.9	0.493
実施例 3	1	86.2	0.481
実施例 4	3	87.0	0.490
比較例 1	166	84.3	0.470
比較例 2	273	90.5	0.485
比較例 3	272	85.9	0.471
比較例 4	446	85.5	0.486

[0025] As shown in a table 1, when a polymerization reaction is performed using the organic peroxide constituent diluted with the dibutyl maleate shown in the examples 1-4, the ullage of the solvent in the obtained vinyl chloride polymer becomes very low, and this solvent is hardly volatilized and eluted the inside of molding, and after molding. Moreover, since a polymerization invert ratio and bulk specific gravity are the same as usual, it does not have an adverse effect on a polymerization or quality. On the other hand, the hundreds of ppm solvent exists in the vinyl chloride polymer manufactured using the organic peroxide constituent diluted with the aliphatic series system hydrocarbon like the examples 1-4 of a comparison. For this reason, there is evil in which this solvent is volatilized and eluted the inside of molding and after molding, or stickiness arises to molding equipment and productivity is reduced with the solvent which remains in mold goods.

[0026]

[Effect of the Invention] As described above, according to this invention, the following outstanding effectiveness is done so. That is, the organic peroxide constituent of this invention can reduce considerably the residual solvent in a vinyl chloride system polymer, without having an adverse effect on a polymerization or quality. Since a solvent is hardly volatilized and eluted from the time of molding, or mold goods by that, an environment-friendly production process and mold goods can be offered. Furthermore, since stickiness of molding equipment is reduced, productivity can be raised conventionally.

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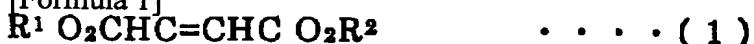
**CLAIMS**

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[Claim(s)]

[Claim 1] The organic peroxide constituent characterized by containing organic peroxide and the compound shown by the following general formula (1) as a solvent for this organic peroxide.

[Formula 1]



(R1 and R2 show the alkyl group of carbon numbers 1-8 among a formula, respectively.)

[Claim 2] The organic peroxide solution which comes to dissolve organic peroxide in the compound shown by the following general formula (1).

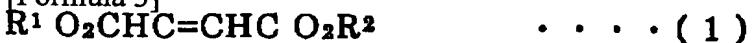
[Formula 2]



(R1 and R2 show the alkyl group of carbon numbers 1-8 among a formula, respectively.)

[Claim 3] The manufacture approach of the vinyl chloride system polymer characterized by carrying out the polymerization of the monomer in which is made to carry out the polymerization of the vinyl chloride monomer to the bottom of existence of the organic peroxide solution which comes to dissolve organic peroxide in the compound of the following general formula (1), or copolymerization is carried out to a vinyl chloride monomer and this, and it deals.

[Formula 3]



(R1 and R2 show the alkyl group of carbon numbers 1-8 among a formula, respectively.)

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(54) 【発明の名称】 布機過酸化物溶液およびそれを使用する塩化ビニル系重合体の製造方法

## (57) 【要約】

【課題】 重合開始剤として使用する有機過酸化物の溶剤が重合や成型加工後の塩化ビニル系重合体の物性に影響を与えず、塩化ビニル系重合体からほどんど揮発及び溶出せず、環境に優しくかつ生産性を上げる有機過酸化物組成物およびそれを使用する塩化ビニル系重合体の製\*

R<sup>1</sup>O<sub>2</sub>CHC=CHC O<sub>2</sub>R<sup>2</sup>

\* 造方法を提供すること。

【解決手段】 有機過酸化物と、該有機過酸化物用の溶剤としての下記一般式(1)で示される化合物とを含有することを特徴とする有機過酸化物組成物。

【化1】

· · · · (1)

(式中、R<sup>1</sup>、R<sup>2</sup>はそれぞれ炭素数1~8のアルキル基を示す。)

(2)

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## 【特許請求の範囲】

【請求項1】有機過酸化物と、該有機過酸化物用の溶剤としての下記一般式(1)で示される化合物とを含有す\*



(式中、R<sup>1</sup>、R<sup>2</sup>はそれぞれ炭素数1~8のアルキル基を示す。)

## 【請求項2】下記一般式(1)で示される化合物に有機※



(式中、R<sup>1</sup>、R<sup>2</sup>はそれぞれ炭素数1~8のアルキル基を示す。)

【請求項3】下記一般式(1)の化合物に有機過酸化物を溶解してなる有機過酸化物溶液の存在下に塩化ビニル★



(式中、R<sup>1</sup>、R<sup>2</sup>はそれぞれ炭素数1~8のアルキル基を示す。)

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は塩化ビニル系重合体を製造するために使用する有機過酸化物溶液に関する。詳しくは、塩化ビニル系重合体をフィルム、シート、パイプ、平板、波板、粧手、レザー、導線の被覆材、床材、被服、自動車部品等の用途に成型する際に重合開始剤として使用する有機過酸化物の溶剤がほとんど揮発及び溶出せず、また成形品においても重合開始剤として使用する有機過酸化物の溶剤がほとんど揮発及び溶出しない塩化ビニル系重合体を提供し得る有機過酸化物溶液、それを用いる上記塩化ビニル系重合体の製造方法に関するものである。

## 【0002】

【従来の技術】塩化ビニル系重合体を製造する際の重合開始剤としては一般的に有機過酸化物が使用されている。その有機過酸化物の多くは、衝撃に敏感であるため、安全に取り扱うため有機過酸化物を溶剤で希釈して輸送、実用しております、その希釈剤としては脂肪族系炭化水素溶剤として例えばシェルゾール(シェルケミカルズジャパン(株)製)、アイソパー(エッソ化学(株)製)、日石アイソゾール(日本石油化学(株)製)、IPソルベント(出光石油化学(株)製)等や芳香族系炭化水素溶剤として例えばトルエン、エチルベンゼン等が使用されている。ところが、これにより、重合開始剤としての有機過酸化物の品質、作業環境及び生産性に悪い影響を及ぼしている。例えば、従来使用されている上記溶剤は塩化ビニル系重合体成型時に成形品から揮発及び溶出したり、成型後に揮発及び溶出したりしておらず、また、成型時に成形品中に残存しているため、成型装置にべつつきが生じ、定期的に整備しなければならず、その都度、製造が中断している。

\*ることを特徴とする有機過酸化物組成物。

## 【化1】

.....(1)

※過酸化物が溶解されてなる有機過酸化物溶液。

## 【化2】

.....(1)

★単量体を重合させるか、あるいは、塩化ビニル単量体およびこれと共に重合される量を重合させることを特徴とする塩化ビニル系重合体の製造方法。

## 【化3】

.....(1)

## 【0003】

【発明が解決しようとする課題】上述したように、脂肪族系炭化水素や芳香族系炭化水素を溶剤として使用した場合、その溶剤は重合や品質に影響しないが成型時及び成形品から揮発及び溶出してしまう。これらの溶剤を除去しようとしても高沸点溶剤であるため除去することが非常に困難であり、除去しようとしても限界がある。また、トルエン、エチルベンゼン等は特定化学物質の環境への排出量の把握等及び管理の改善の促進に関する法律(PRTR法)でその使用が規制されているように、成形品から該溶剤が揮発及び溶出し、また廃液中に含有しているため、環境に対して悪影響を及ぼす。また、溶剤が成型時に成形品中に残存しているため成型装置にべつつきが生じ、生産性を低下させている。そして、このような課題に対して従来解決策が提示されていない。このような観点から、重合反応や成形品の品質に影響を与える、また成型時及び成形品からの溶剤の揮発及び溶出の低減された塩化ビニル系重合体を製造し得、かつ成型装置のべつつきをなくし、生産性を上げる有機過酸化物溶液を提供すること、それによる塩化ビニル系重合体の製造方法を提供することが本発明の課題である。

## 【0004】

【課題を解決するための手段】本発明者らは上記の課題の解決を図るべく鋭意検討した結果、有機過酸化物の溶剤として下記一般式(1)で示される化合物を使用することによって、衝撃に敏感な有機過酸化物を安全に取り扱うことができ、重合や品質に影響を与えず、成型時及び成形品からの溶剤の揮発及び溶出を低減し、更には成形品中に残存する溶剤量を低減し、かつ成型装置のべつつきをなくすことにより生産性を上げることができることを見出した。すなわち、本発明は、有機過酸化物と、該有機過酸化物用の溶剤としての下記一般式(1)で示される化合物とを含有溶剤とする有機過酸化物組成物に関する。

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ルロース、ヒドロキシエチルセルロース、ヒドロキシブロビルセルロース、ヒドロキシプロビルメチルセルロース等の水溶性セルロースエーテル、水溶性あるいは油溶性の部分けん化ポリビニルアルコール、アクリル酸亜台体、ゼラチン等の水溶性高分子、ソルビタンモノラウレート、ソルビタントリオレート、グリセリントリステアレート、エチレンオキシドプロピレンオキシドブロックコポリマー等の油溶性乳化剤、ポリオキシエチレンソルビタンモノラウレート、ポリオキシエチレングリセリンオレート、ラウリン酸ナトリウム等の水溶性乳化剤などを1種又は2種以上の組み合わせて使用することもできる。更にこの重合系では必要に応じて、塩化ビニル系の重合に適宜使用される重合調整剤、遮離移動剤、pH調整剤、グル化改良剤、帯電防止剤、架橋剤、安定剤、充填剤、酸化防止剤、緩衝剤、スケール防止剤等を添加することも任意である。

【0011】有機過酸化物、即ち重合開始剤の使用量は塩化ビニル系単量体100重量部に対して、純品換算で0.01～2重量部、好ましくは0.001～1重量部である。0.001重量部未満では重合速度が低下し、また2重量部を超えると重合速度が大きくなり、その制御が困難になる。

【0012】重合温度は、重合方法や単量体の組み合せによって異なる一様ではないが、10～80°C、好ましくは30～70°Cである。10°C未満では重合時間が長くなる傾向にあり、反応の完結が難しく、重合時間が長くなり生産性が低下する。80°Cを超えると、反応速度が著しく大きくなり重合反応の制御が困難となり、重合開始剤の寿命が短くなり、高転化率に到達することが困難となり好ましくない。

【0013】

【実施例及び比較例】以下実施例及び比較例を示して本発明を具体的に説明するが、本発明はこれら実施例に限定されるものではない。

【0014】2Lのステンレス製オートクレーブに、イオン交換水1300mLとポリビニルアルコール0.8gを入れて溶解し、次に活性酸素ベースで36.5ppmの有機過酸化物組成物(後述)を添加し、オートクレーブ内を窒素ガスで十分に置換し、その後オートクレーブ内を真空に密栓した。塩化ビニル単量体550gを加熱後、オートクレーブに充填した。オートクレーブを温水で加温して、内部温度を57°Cに保ちながら重合を行い、圧力が0.5気圧低下した後、1時間後に重合を終了させた。重合終了後、オートクレーブを冷却し、未反応の塩化ビニル単量体を除き、得られた白色の結晶を300mLのイオン交換水で回洗浄した後、55°Cで乾燥した。溶剤の残存量、重合転化率、かさ比重の測定を行った結果を表1に示した。

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【0015】[溶剤の残存量] 乾燥して得られた塩化ビニル重合体5gを100mLのテトラヒドロフランに添加し、完全に溶解させる。塩化ビニル重合体が完溶したテトラヒドロフラン溶液をガスクロマトグラフィーで分析し、塩化ビニル重合体中の溶剤含量を算出した。

【0016】[実施例1] 有機過酸化物組成物として1-ブチルバーオキシネオデカノエートのジブチルマレート70%溶液を塩化ビニル単量体に対し796ppm添加し重合を行った。

10 【0017】[実施例2] 有機過酸化物組成物としてジ(2-エチルヘキシル)バーオキシジカルボネートのジブチルマレート70%溶液を塩化ビニル単量体に対し1130ppm添加し重合を行った。

【0018】[実施例3] 有機過酸化物組成物としてα-クミルバーオキシネオデカノエートのジブチルマレート70%溶液を塩化ビニル単量体に対し450ppm、ジ(2-エチルヘキシル)バーオキシジカルボネートのジブチルマレート70%溶液を塩化ビニル単量体に対し620ppmそれぞれ添加し重合を行った。

20 【0019】[実施例4] 有機過酸化物組成物として3-ヒドロキシ-1,1-ジメチルブチルバーオキシネオデカノエートのジブチルマレート50%溶液を塩化ビニル単量体に対し590ppm、ジ(2-エチルヘキシル)バーオキシジカルボネートのジブチルマレート70%溶液を塩化ビニル単量体に対し620ppmそれぞれ添加し重合を行った。

【0020】[比較例1] 実施例1の有機過酸化物組成物の代わりに1-ブチルバーオキシネオデカノエートの脂肪族系炭化水素70%溶液を添加し重合を行った。

30 【0021】[比較例2] 実施例2の有機過酸化物組成物の代わりにジ(2-エチルヘキシル)バーオキシジカルボネートの脂肪族系炭化水素70%溶液を添加し重合を行った。

【0022】[比較例3] 実施例3の有機過酸化物組成物の代わりにα-クミルバーオキシネオデカノエートの脂肪族系炭化水素70%溶液、ジ(2-エチルヘキシル)バーオキシジカルボネートの脂肪族系炭化水素70%溶液を添加し重合を行った。

40 【0023】[比較例4] 実施例4の有機過酸化物組成物の代わりに3-ヒドロキシ-1,1-ジメチルブチルバーオキシネオデカノエートの脂肪族系炭化水素50%溶液、ジ(2-エチルヘキシル)バーオキシジカルボネートの脂肪族系炭化水素70%溶液を添加し重合を行った。

【0024】

【表1】

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	重合体中の溶剤 残存量[ppm]	重合転化率 [%]	かさ比重 [g/ml]
実施例 1	2	84.3	0.475
実施例 2	1	89.9	0.493
実施例 3	1	86.2	0.481
実施例 4	8	87.0	0.490
比較例 1	166	84.3	0.470
比較例 2	278	90.5	0.485
比較例 3	272	85.9	0.471
比較例 4	446	85.5	0.486

【0025】表1に示したように、実施例1～4で示したジブチルマレートで着脱した有機過酸化物組成物を使用して重合反応を行った場合には、得られた塩化ビニル重合体中の溶剤の残存量はきわめて低くなり、成型中や成型後に該溶剤が揮発及び溶出することがほとんどない。また、重合転化率やかさ比重は従来と同様であるため、重合や品質には悪影響を与えない。一方、比較例1～4のように、脂肪族系炭化水素で着脱した有機過酸化物組成物を使用して製造した塩化ビニル重合体には数百ppmの溶剤が存在している。このため、成型中や成型後に該溶剤が揮発及び溶出したり、成形品中に残存してい

る溶剤により、成型装置にべとつきが生じ生産性を低下させるという弊害がある。

#### 【0026】

【発明の効果】以上記述したように、本発明によれば次のような優れた効果を奏する。すなわち、本発明の有機過酸化物組成物は重合や品質に悪影響を与える事なく、塩化ビニル系重合体中の残存溶媒をかなり低減できる。そのことにより成型時や成形品から溶剤がほとんど揮発及び溶出しないため環境に優しい製造工程や成形品を提供することができる。更に成型装置のべとつきが低減されるため従来より生産性を上げることができる。

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